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HIGH PRESSURE SYNTHESES INVOLVING RARE EARTHS

BY H. TRACY HALL

In the commercial field, the use of high pressure simultaneously with high temperatue for the synthesis of drugs, diamonds and semicondutors provides some attractive economic possibilities. Some problems connected with determining what materials to synthesize are discussed and the synthesis of semiconducting rare earth antimonides and sulfides are given as an example of one successful approach to these problems.

Rare Earth Diantimonides

The rare earth elements comprise a unique series in which the chemistry of the atoms is very similar but in which the atom and ion sizes (nominally the +3 state) decrease regularly in what is known as the lanthanide contraction. Elements preceeding Gd are called light rare earths while ele-

Table 1 The rare earth elements

Element	Atomic number	+3 Ionic radius (Å)
Sc	21	0.68
Y	39	0.910
La	57	1.061
Ce	58	1.034
Pr	59	1.013
Nd	60	0.995
(Pm)	61	0.979
Sm	62	0.964
Eu	63	0.950
Gd	64	0.938
Tb	65	0.923
Dy	66	0.908
Ho	67	0.894
Er	68	0.881
Tm	69	0.869
Yb	70	0.858
Lu	71	0.848

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1) H. T. Hall, *J. Chem. Ed.*, **38**, 484 (1961)
2) H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960)
3) H. T. Hall, *ibid.*, **29**, 267 (1958)

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ments following Gd are called heavy rare earths. Yttrium, atomic number 39, while not strictly a lanthanide (elements 57～71), is found in nature with the lanthanides because of similar chemistry. In size, it ranks near Dy and often positions near this element in a series of size dependent properties. Scandium, atomic number 21, is also often considered with the lanthanides but is much smaller than Lu, the smallest of the lanthanides. Promethium is a synthetic, radioactive rare earth. Not found in nature, it is generally unavailable. Symbols for synthetic elements are enclosed in parentheses *i.e.*, (Pm). Table 1 lists the rare earth elements and the radii of their +3 ions along with their atomic numbers.

Recently, a BYU graduate student, N. L. Eatough[4], while searching the literature for ideas, came accross the work of R. Wang and H. Steinfink[5] on the synthesis of some rare earth diantimonides. These compounds are of interest because of their semiconducting properties. Wang and Steinfink succeeded in preparing some RSb_2 (R stands for any rare earth element) compounds of $LaSb_2$-type orthorhombic crystal structure in the interval from La through Sm. However, they were unable to synthesize any compounds beyond Sm by the technique employed which consisted of subjecting a mixture of rare earth metal and Sb powders to high temperature in an evacuated, sealed tube. This presented a challenge for Eatough to see if the series could be extended to heavier rare earths by the use of high pressure and high temperature. He was successful and consequently opened the door to a number of rare earth syntheses.

When Wang and Steinfink could not prepare Gd and heavier diantimonides, they postulated that the sizes of Gd and the heavier rare earths are too small for the crystal to be stable. Specifically, they noted that the shortest bond distance in $SmSb_2$ is 2.79 Å which is substantially shorter than the 2.90 Å bond in elemental antimony and is also shorter than the shortest Sb-Sb bond previously known of 2.81 Å which occurs in CdSb and in ZnSb. They reasoned that the repulsion in the short Sb-Sb bond (there is also a long Sb-Sb bond in the structure) becomes critical at Gd and causes the $LaSb_2$-type structure to become unstable and incapable of synthesis.

However, aided by high pressure, Eatough synthesized $GdSb_2$ and also the next heavier member of the series $TbSb_2$. He also prepared the light rare earth compound $PrSb_2$ which Wang and Steinfink had not attempted. These new compounds are also of $LaSb_2$-type structure. The short Sb-Sb bond in $TbSb_2$ is only 2.76 Å which is now the shortest Sb-Sb bond known. It is quite probable that the new compounds are only metastable at room pressure and temperature. These compounds are prepared in a region of pressure and temperature where thermodynamic stability prevails and are then quenched to room temperature before pressure is released. On release of pressure the atoms maintain their essential high pressure configuration although there is, no doubt, considerable strain in the crystal due to the very short Sb-Sb bonds.

When Eatough attempted the preparation of diantimonides beyond Tb, he made them but a change in crystal structure occurred. Apparently the Sb-Sb bond had become too short to be maintained even by application of high pressure so an adjustment had to be made in the atomic arrange-

4) N. L. Eatough, PhD Dissertation, Brigham Young Univ. (1968)

5) R. Wang and H. Steinfink, *Inorg. Chem.*, 6, 1685 (1967); R. Wang, PhD Dissertation, Univ. of Texas (1967)

ment. It has not been possible to obtain single crystals for use in x-ray diffractometry to establish the details of this new structure. For the present, the crystalline arrangement is referred to as the high pressure orthorhombic (HPO) structure. The HPO diantimonides synthesized beyond Tb were those of Dy, Ho, Er, Tm, and Y.

The HPO structure was also found, at appropriate synthesis pressures and temperatures, for $GdSb_2$ and $TbSb_2$. These two compounds, then, can exist in the former $LaSb_2$-type structure of the lighter rare earths or as polymorphs in the HPO structure of the heavy rare earths.

It might be well at this time to point out the distinction between a synthesized *polymorph* and a synthesized *compound*. If a chemical substance is already known in one crystalline form and a new crystalline form of the same chemical composition is made, this is referred to as the synthesis or preparation of a polymorph. If, on the other hand, the chemical combination did not previously exist in any form, the making of this chemical entity is referred to as the synthesis of a new compound. Technically, all crystalline forms of the same chemical composition are polymorphs but there are no polymorphs until a second crystalline form of a substance has been discovered.

Eatough was the first to synthesize new rare earth A_xB_y compounds by application of high pressure. However, H. R. Hockstra and K. A. Gingerich[6] preceeded him in the use of high pressure to prepare rare earth polymorphs. These workers, using pressures in the range of 25~40 kbar at temperatures of 900~1,020°C, transformed a known cubic phase of R_2O_3 into a monoclinic phase in the instance of Ho, Er, Tm, Yb, and Lu. The monoclinic phase was previously known only for Sm, Eu, Gd, and Dy.

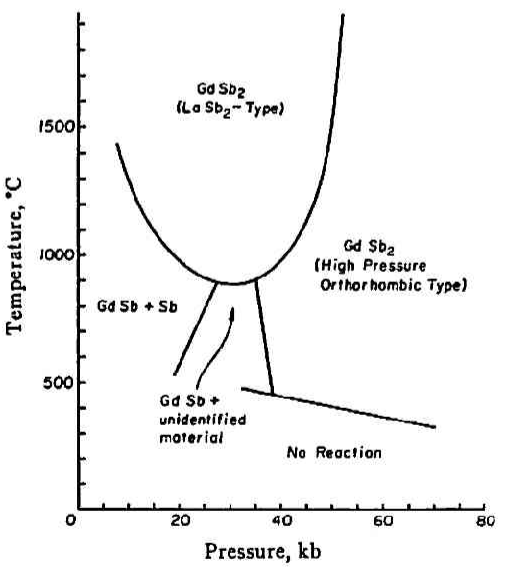

Fig. 1 Reaction product diagram for Gd+2Sb

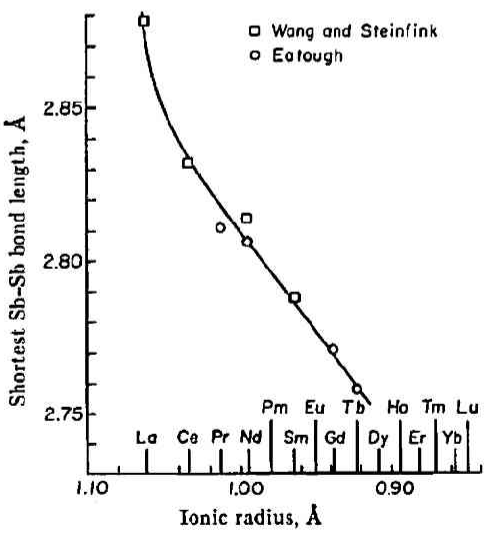

Fig. 2 Short Sb-Sb length in $LaSb_2$-type rare earth diantimonides

6) H. R. Hocstra and K. A. Gingerich, *Science*, 146, 1164 (1964)

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The rarth earth diantimonides prepared by Eatough are silver-gray in color, stable in air, but react slowly with water. They are semiconductors. In their synthesis, powders of the rare earth and of antimony in 1 : 2 atomic proportions are mixed with each other. The mixture is then subjected to appropriate pressure and temperature conditions which are determined by systematic trial and error and plotted as a "reaction product diagram." This diagram shows the region that will produce the diantimonide upon quenching after the reactants are first subjected to a P, T point within the region. The diagram for the Gd+2Sb mixture is shown in Fig. 1. The reaction product diagram for Tb+2Sb is similar to Fig. 1 but the pressure range over which the $LaSb_2$-type $TbSb_2$ can be synthesized narrows to a slender region of 6 kbar maximum width centered at 40 kbar and extending from 950 to 1,800°C. At Dy, the slender region thins to zero width and $LaSb_2$-type $DySb_2$ cannot be synthesized.

A plot of the short Sb-Sb bond length in the $LaSb_2$-type rare earth diantimonides is shown in Fig. 2. These compounds form an interesting series just entering the metallic conduction category. Wang and Steinfink estimated the metallic bond character in $LaSb_2$ at 93% and in $SmSb_2$ at 96%. Extending their line of reasoning to $TbSb_2$ would indicate that the metallic bond character of this new member of the series is about 98%.

Rare Earth Polysulfides

Rare earth sulfides have also become of interest because of their solid state electrical properties. Some polysulfides of nominal composition RS_2 were prepared using sealed tube techniques by J. Flahaut, M. Guittard and M. Patrie[7] and also by S. A. Ring and M. Tecotsky.[8] Flahaut *et al.* found La, Ce, Pr, Nb, and Sm to be of cubic crystal symmetry of the prototype LaS_2-type. They found the polysulfides of Eu, Gd, and Y to be tetragonal and non-stoichiometric, having a lower composition limit of $RS_{1.90}$ compared to the stoichiometric or ideal compostion RS_2. They could not synthesize ErS_2 and YbS_2. Ring *et al.* succeeded in synthesizing the polysulfides of Tb, Ho, and Er(also tetragonal and non-stoichiometric), but found it impossible to synthesize TmS_2. It was neccessary to lower the temperature upon progressing to the heavier rare earths or the RS_2 compound would not form. A higher sulfur vapor pressure was also needed. In sealed tube techniques, however, reduced temperature results in a lower sulfur pressure.

To A. W. Webb, another BYU graduate student[9], it seemed that high pressure would extend the stabilitiy zone of the RS_2 compounds to higher temperatures while simultaneously maintaing a high sulfur pressure and make it possible to synthesize the heavier rare earth polysulfides. His reasoning was correct and he synthesized three new compounds, the Tm, Yb, and Lu polysulfides of tetragonal symmetry. In addition, he extended the previously known LaS_2-type cubic compounds, ending at Sm, through the heavy rare earths. This resulted in eight polysulfide polymorphs; namely, those of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

7) J. Flahaut, M. Guittard and M. Patrie, *Bull. Soc. Chim. Fr.*, Series 5, 26, 1917 (1959)
8) S. A. Ring and M. Tecotsky, *Inorg. Chem.* 3, 182 (1964)
9) A. W. Webb, PhD Dissertation, Brigham Young Univ. (1965)

The known polyselenides, RSe_2, similarly parallel the polysulfides and by the use of high pressure, high temperature technique, Webb also synthesized the heavy rare earth compounds $TmSe_2$, $YbSe_2$, and $LuSe_2$ to complete this series.

The reaction product diagrams for the R+2S series are interesting. That for Gd+2S is shown in Fig. 3. As in the case of the synthesis of the diantimonides, the product named in the *P-T* region outlined is the one that will be obtained on quenching the reactants from a *P*, *T* point within this region. For the heavier rare earth polysulfides beyond Gd, the reaction product diagram is similar to that for Gd except that the minimum pressure boundary for the formation of the cubic phase is shifted in a regular manner to the right (to higher pressure). This minimum formation pressure is plotted as a function of the ionic radius of the rare earths as is shown in Fig. 4.

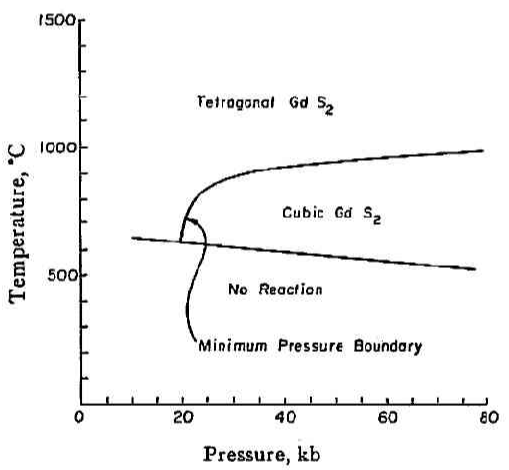

Fig. 3 Reaction product diagram for Gd+2S

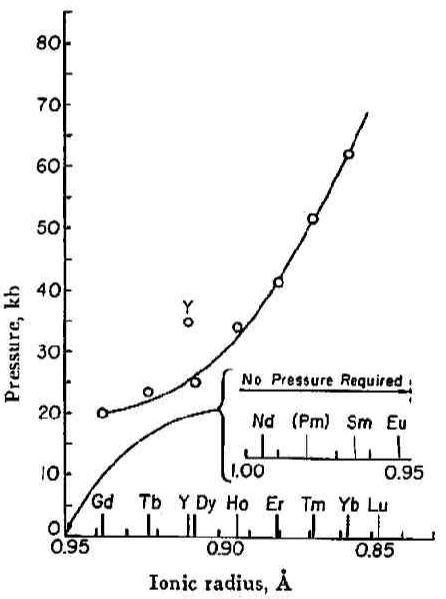

Fig. 4 Minimum formation pressure at approximately 650°C for RS_2 cubic compounds (LaS_2-type)

4*f* Bonding in Compounds

Electronically, the lanthanides are ideally characterized by an inner, 4*f* energy level or shell which begins to fill by adding one electron at Ce and continues to fill by adding an additional electron with each increase in atomic number until at Lu the 14th and final electron is added to completely fill the shell. The 4*f* shell is considered to be deeply buried and ideally does not enter into chemical bonding. However, recent ideas and experimental evidence suggest that the 4*f* electrons do participate to some extent in bonding. This is particularly true in the lighter rare earths but is thought to occur under high pressure in the heavy rare earths. The 4*f* bonding is apparently responsible for

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subtle crystal structure changes which occur on progressing through the series of rate earth metals from La to Lu. K. A. Gschneidner, Jr. and R. M. Valletta have recently discussed this matter[10] and have suggested a fertile field of research exists in the area of the effect of high pressure on rare earth alloys and compounds. They further suggest a test for 4*f* contribution to the bonding in a series of rare earth compounds wherein pressure determines which of two polymorphs will form. If (at a fixed temperature), increasing pressure is required with *increasing* atomic number to form one of the polymorphs, then 4*f* electrons are contributing to the bonding. If increasing pressure is required with *decreasing* atomic number, then 4*f* bonding is not involved.

The curve in Fig. 4 essentially represents the pressure phase boundary at fixed temperature (about 650°C) between tetragonal RS_2 to the left of the curve and cubic RS_2 to the right of the curve. Since increasing pressure is required to form the cubic polymorph as atomic number increases, 4*f* bonding is involved. Note that Y does not fit on the curve. Its formation required a pressure higher than expected. There can be no 4*f* bonding in Y and this may account for the anomaly.

Conclusion

Other synthesis work at BYU includes research on rare earth sesquisulfides and compounds of tellurium and of tin, some of this by graduate student J. F. Cannon[11]. As of this writing, forty new rare earth compounds or polymorphs have been prepared. In this research, the synthesis situation is almost always the same. A series of rare earth conpounds previously prepared by other workers utilizing sealed tube techniques ends at some critical point as ionic size decreases. The application of high pressure then makes it possible to extend the series to the heavier rare earths and also usually leads to the synthesis of a series of new polymorphs of the same chemical composition.

Two effects may be at work in these syntheses. Firstly, the compression of the heavy rare earth atoms brings the 4*f* electrons into play so that these atoms behave more like the lighter rare earth elements. Secondly, in the instances studied, the rare earth is less compressible than the entity with which it is being combined. Consequently, pressure reduces the size of this entity more than it reduces the size of the rare earth. Relative sizes are thus restored to those prevailing for the lighter rare earths at atmospheric pressure.

The reverse situation in which the rare earth is more compressible than the atom with which it is combined has not been studied. This might occur when the rare earth is combined with such atoms as Be, C, N, and the group VIII metals. For a series in which the rare earth compound becomes unstable as La is approached from the heaver end of the series (due to the increasing size of the rare earths in this direction), high pressure should extend the series toward La. High pressure should also increase the natural 4*f* contribution to bonding in the lighter rare earths. This could lead to an increase in polymorphic forms and to other interesting effects. Whether or not any of the syntheses

10) K. A. Gschneidner, Jr. and R. M. Valletta, *Acta Met.*, **16**, 477 (1968)
11) J. F. Cannon, PhD Dissertation, Brigham Young Univ. (1969)

discussed above will lead to a commercial end can not presently be answered. But compounds once only imagined (and some not imagined) are now known to exist and that of itself constitutes the first step.

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